A promising approach to the kinetics of crystallization processes: the sample controlled thermal analysis

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Abstract

Constant Rate Thermal Analysis (CRTA) method implies controlling the temperature in such a way that the reaction rate is maintained constant all over the process. This method allows determining simultaneously both the kinetic parameters and the kinetic model from a single experiment, since the shape of the CRTA α-T curves strongly depends on the kinetic model. CRTA method has been developed in the market only for thermogravimetric and thermodilatometric systems and, therefore, its use has been limited until now to the kinetic study of processes involving changes in mass or size of the samples, respectively. In order to overcome this obstacle, a method has been developed in the present work for using the DSC signal for controlling the process rate in such a way that CRTA would be applied to the kinetic analysis of either phase transformations or crystallizations. The advantages of CRTA for performing the kinetics of crystallization processes have been here successfully demonstrated for the first time after selecting the crystallization of zirconia gel as test reaction.

Keywords: kinetics; crystals/crystallization; differential thermal analysis; reaction rate, zirconia

1. Introduction

Sample controlled thermal analysis (SCTA) methods have been proved to be of the most interest in materials science.[1-5] In these methods the sample itself determines the heating profile. The instrument uses an analogical output representative of the rate of the process as a control signal. Thus, in a typical SCTA experiment, the sample is heated until the reaction rate reaches a preset value of the control signal that trigger a change of the profile temperature that forces to the process to fit the values of the controlling signal generated by a preset controlling atgorithm.[3, 4, 6, 7]

Constant Rate Thermal analysis (CRTA), developed by Rouquerol and the Pauliks,[8, 9] is the most widely used SCTA method, based on the control of the process temperature in such a way that the reaction rate is maintained constant all over the process.[3]

The interest of SCTA comes from the possibility of controlling the rate of the process at values low enough for achieving that the temperature and pressure gradients within the sample are negligible. Therefore, the heat and mass transfer phenomena are minimized in order to obtain reliable kinetic parameters of the forward reaction.[10, 11] Moreover, other important advantage of SCTA is its high resolution power for the discrimination between kinetic models of solid state reactions, especially in comparison with conventional non-isothermal methods. Thus, while it is not possible to obtain information about the kinetic mechanism of the processes from the shape of curves registered under linear heating rate conditions, the shape of SCTA curves is related to the kinetic models, and consequently, valuable information can be obtained from the shape of the curves regarding the mechanism of the process.[4, 12, 13] These methods can also improve the resolution of overlapping processes and reveal the lowest temperature ranges over which processes can occur.[14-16] SCTA has been applied for the preparation of different kinds of materials. It has been shown that CRTA method has advantages for the synthesis of ceramics[17-21] and glasses,[22] and materials with controlled texture and structure,[23-28] including the preparation of different kinds of catalysts.[14, 29, 30] It has also been used for the thermal analysis of a wide range of reactions, such as dehydrations and dehydroxylations,[31-34] denitrations[35] and

decarbonations.[36, 37] Moreover, CRTA experiments have been included in kinetic studies of thermal decomposition of materials, mainly carbonates,[4, 11, 38-42] polymers,[13, 43-45] polymer nanocomposites,[46] but also other compounds,[47-49] in order to clarify the kinetic model followed by the reactions. Interestingly, SCTA has also applications in quantitative characterization,[16, 50] and even has been used in sintering studies.[51, 52] In all these studies, the change in mass, length, pressure or composition of a specific gas generated during the reactions have been used as control signals representative of the reaction rate. However, for crystallization processes no mass change or gasses are generally generated in the process and therefore conventional SCTA instruments are useless. In principle, the heat flow associated to the process is a very good alternative for controlling the rate of the process. Very few studies have used this approach. Probably, the first one is the so called "Smith Thermal Analysis" that uses the temperature difference between the sample and the reference for monitoring the rate of the process.[53] Newer approaches are those of Paulik et al.[54, 55] and Charsley et al.[56] that use the DTA signal of a simultaneous TG-DTA equipment and a modified DSC cell, respectively. These instruments have been used for studying phase transformations in metallic alloys,[57] phase changes in inorganic compounds,[54] or curing of epoxy resin.[56] However, up to the best of our knowledge, this method has not been yet used for the kinetic analysis of crystallization or phase transformations of solids.

Crystallization processes are exothermic and produce a significant increase in sample temperature. Thus, unusual peak shapes that can be difficult to analyze depending on the heat flow associated to the crystallization process are commonly observed.[58] These effects can be avoided using the SCTA methodology since a control of the reaction rate minimizes the heat transfer phenomena. Moreover, it is well known that DSC baseline largely changes depending on the heating conditions, because a change in specific heat often occurs after the sample goes through crystallization, which makes the integration of a peak which has a baseline shift difficult and less accurate. Taking into account that using CRTA the transformation rate is maintained constant, the change in the baseline of the DSC is also expected to be constant and therefore easy to extract from the measured data to obtain the data for kinetic calculations.

The aim of this work is to explore the possibilities of SCTA, and in particular of CRTA, for the first time for studying kinetics of crystallization processes using the heat flow signal for monitoring the process, as an alternative to conventional linear heating or isothermal conditions.[59-64] The potential of CRTA in crystallization studies is demonstrated by the analysis of the crystallization of a dried zirconia gel.

2. Materials and methods

Commercially available zirconium (IV) hydroxide purchased from Sigma-Aldrich (product number 464171-500G, 97% pure) was used to perform the study. The samples were previously dried at 473 K during 10 hours, in such a way that the starting material was amorphous anhydrous zirconium (IV) oxide. The experiments were carried out in a simultaneous TG/DSC Instrument (Q600 SDT, TA Instruments, Crawley, UK). Although the instrument is able to perform differential scanning calorimetry and thermogravimetric analysis, the DSC was the only signal used in this work to study the kinetics of crystallization of the anhydrous zirconium (IV) oxide, since the sample was totally dehydroxylated prior to crystallization.

DSC curves were recorded in open platinum pans under nitrogen flow (100 cm^3 min^{-1}), employing both the CRTA method and the conventional rising temperature method. A custom method, described in detail in the Results and discussion section, was created using the instrument software to perform the CRTA experiment. Typical sample size was ~20 mg.

3. Theoretical

The reaction rate of solid-state processes in conditions far from equilibrium is described by the equation:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}f(\alpha) \qquad (1)$$

where α is the degree of conversion, t the time, T the absolute temperature, A is the Arrhenius pre-exponential factor, E the activation energy, R the gas constant and f(α) accounts for the reaction rate dependence on α. For DSC experiments, the conversion is calculated integrating and normalizing the experimental curves. Then, the reaction rate is obtained differentiating the curves with respect to the time. The kinetic equations f(α) are algebraic expressions associated with physical ideal models which consider geometrical and driving forces for the solid state processes. Table 1 presents the most common expressions found in literature.

Equation 1 can be rewritten, taking logarithms, in the following form:

$$ln\left(\frac{d\alpha/dt}{f(\alpha)}\right) = \ln(A) - \frac{E}{RT} \qquad (2)$$

This equation can be used regardless the thermal schedule employed to record the data. The plot of the left hand side of equation (2) versus the reciprocal of the temperature leads to a straight line only if the proper f(α) function is selected, which implies and advantage over other model-fitting methods based on the integral form of the kinetic equation. By means of this differential model-fitting method, the activation energy is obtained from the slope of such line and the preexponential factor from the intercept.

For experiments performed under CRTA conditions the reaction rate, dα/dt, is maintained at a constant value, C, and equation (2) can be written as follows:

$$ln\frac{1}{f(\alpha)} = ln\frac{A}{C} - \frac{E}{RT} \qquad (3)$$

It has been previously shown that, while it is impossible to obtain the activation energy and discriminate the mechanism of the process from a single experiment recorded in linear heating

conditions, CRTA experiments are able to distinguish between the kinetic models presented in Table 1, i.e. n-order, Avrami-Erofeev and diffusion, due to the correlation between the temperature-time profile of CRTA curves and the mechanism of the process.[12] Figure 1 shows, as examples, α-T curves simulated using the same activation energy of 125 kJ mol^{-1} and pre-exponential factor of 10^{12} min^{-1} and considering the kinetic models in Table 1. Figure 1a presents curves constructed assuming a linear heating rate of 5 K min^{-1} and Figure 1b shows CRTA curves at a constant rate of 10^{-3} min^{-1}. The simulation was carried out employing the Runge-Kutta method by means of the Mathcad software.

The curves simulated under linear heating rate conditions in Figure 1a are sigmoidal in shape regardless the mechanism of the process. On the other hand, it is clear from Figure 1b that the shape of CRTA curves is strongly dependent on the kinetic model. Thus, the α-T plots of reactions controlled by the diffusion (like D3) have a sigmoidal shape, while the plots of interphase boundary controlled reactions (like F1 and R3) are concave. Finally, in case of reactions controlled by a random nucleation and nuclei growth, the α-T profile starts with a rise in temperature until the beginning of the reaction and then it backs on itself until reaching a given value of the reacted fraction at which the heating is resumed again, as Figure 1b shows. This quite unconventional shape of the α-T plot makes CRTA an outstanding procedure for performing the kinetic analysis of phase transitions and crystallization processes, which generally follow an Avrami-Erofeev mechanism. Moreover, the above analysis suggests that just a glance to the shape of the CRTA curve permits to outline the kinetic model even before to perform any numerical kinetic analysis.

4. Results and discussion

Figure 2 presents an experimental DSC peak for the thermal crystallization of the dried zirconia gel registered at the conventional heating rate of 1 K min^{-1}. The degree of conversion at a given

temperature (α_i) is calculated dividing the area under the curve at this temperature (A_i) by the total area enclosed by the curve (A_T).

The integral curve, in Figure 3, has a sigmoidal shape and can be well fitted with different models employing the differential model-fitting method. Therefore, the kinetic model obeyed by the process and the kinetic parameters cannot be unambiguously determined employing one curve registered in linear heating rate conditions. Consequently, a reliable kinetic analysis can only be performed if a set of curves are recorded at different heating rates.[65]

A custom method was created using the Q600 SDT instrument control software to perform the CRTA experiment. A flowchart of the CRTA experiment is shown in Figure 4. The procedure basically consists in comparing the real-time DSC signal and the preset (set point) heat flow. The method takes advantage of the use of the set point parameters defined in the TA control software. The following method was used:

STEP 1. Abort next seg if W g^{-1} < *minimum heat flow*

STEP 2. Ramp *cooling rate in* °C/min to *minimum temperature* °C

STEP 3. Abort next seg if W g^{-1}> *maximum heat flow*

STEP 4. Ramp *heating rate* in °C/min to *maximum temperature* °C

STEP 5. Repeat 1 until *maximum temperature* °C

Values of maximum and minimum heat flows, maximum and minimum final temperatures and heating and cooling rates should be modified according to the sample or process. The procedure consists of heating the sample at a constant heating rate until the heat flow (and, therefore, the rate of the process) exceeds a pre-set maximum heat flow. At this point the temperature increase stops and the system starts to cool down at a constant cooling rate until the heat flow reaches a pre-set minimum heat flow, when the heating is resumed. Thus, the program oscillates between heating and cooling. If both minimum and maximum heat flows are pre-set at very close values, the rate of the process will be, basically, constant along the entire process.

Figure 5 shows the experimental plot of the heat flow and temperature versus time, as obtained for the thermal crystallization of the dried zirconia gel under CRTA conditions. The heating and cooling rates were set at 1 K min^{-1} and 5 K min^{-1} respectively, and the set point was a heat flow of 0.15 W g^{-1}. The temperature increased until the heat flow reached the value previously selected. When this value was reached, the custom method created in the software forced the instrument to decrease the temperature, and then followed an irregular profile that depends on the kinetic model followed by the process. Thus, the heat flow, which is equivalent to the rate of the process, is approximately constant as observed in the figure, and a linear baseline shift was considered for the kinetic analysis.

Figure 6 compares the DSC traces for the experiments performed in conventional linear heating rate and in CRTA conditions. For conventional heating rate experiments, the heat is released in 30 minutes when the sample is heated at 1 K min^{-1} and changes with time as presented in Figure 6b. For linear heating rate experiments the temperature gradients and thermal inertia should be taken into account in DSC (or DTA) analysis since they always exist in real measurements. These phenomena produce bad fittings between the maximum reaction rates and significant errors in the calculations of the degree of conversion, that are more appreciable as the sharpness of the peak increases due to the exothermicity of the process or the heating rates employed in the experiments.[66] On the other hand, for the CRTA experiment, the heat is released on longer times and is approximately constant along the process (note the scale for CRTA in Figure 6b). For these reasons, the effects in the sample temperature produced by the exothermicity of the crystallization process can be avoided by using the CRTA methodology, since a control of the rate of the process minimizes the heat transfer phenomena.

Figure 7a presents the conversion, calculated integrating and normalizing the experimental CRTA curve, the rate of the process and the temperature versus time. The experimental conditions used to perform the CRTA experiment gave a rate of the process of 8×10^{-3} min^{-1}, as may be seen in the figure. The rate of crystallization is constant and the conversion fits a straight line as a function of time. The temperature increases in the initial part of the process, followed by a decrease until a certain value of the conversion, with a final rising until completing the

process. Hence, the curve falls back on itself to maintain the constant rate of crystallization, which creates a minimum in the curve. From the α-T curve presented in Figure 7b, it is clear that the minimum appears at α ~ 0.5 that is characteristic of Avrami-Erofeev nucleation and growth mechanisms. However, it is important to take into account that this procedure for determining the kinetic model can only be employed if the process is single step or composed by separable individual processes.[3, 43]

The differential model-fitting method, applied to the CRTA curve to obtain the activation energy and preexponential factor, unambiguously confirmed that only the nucleation and growth models are able to fit the CRTA curve, as shown in Figure 8. The best fit is achieved for the A4 kinetic model, with activation energy and preexponential factor of 220 kJ mol^{-1} and 5.90 × 10^{15} min^{-1}, respectively. These values are slightly lower than that obtained by the fit of the curve registered under linear heating rate conditions (Figure 3) with the A4 kinetic model. This model is characterized by a constant rate of homogeneous nucleation during the process and subsequent growth of the nuclei in three dimensions.

The calculated kinetic parameters (activation energy and preexponential factor) were checked using these parameters to simulate a CRTA curve assuming the same reaction rate (8 × 10^{-3} min^{-1}) and considering the obtained A4 kinetic model. The simulation was carried out employing a numerical integration of the general kinetic equation. It is clear in Figure 7 that the reconstructed and experimental α-T curves overlap, validating the kinetic parameters obtained by the differential model-fitting method.

Therefore, a CRTA experiment allows discriminating between the kinetic models, and a single curve can be used to obtain reliable kinetic parameters, with the exception of n-order processes.[4, 42] On the contrary, for linear heating rate experiments, the kinetic parameters could not be determined from a single curve.

The kinetics of crystallization of amorphous materials has been usually studied in literature assuming nucleation and growth mechanism as the model followed by the process. However, it is important to take into account that the methodology here employed implies that the results are obtained without any previous assumption about the kinetic model or the activation energy,

since the different models have been tested by means of the differential model-fitting method in order to obtain the model obeyed by the process. The values of activation energy obtained are in good agreement with previously reported results for the crystallization of zirconia gels prepared by precipitation methods,[67, 68] but below those reported for zirconia gels synthetized by other methods, such as from zirconium peroxide[69] or freeze-dried precursors.[70]

5. Conclusions

The use of CRTA for kinetic analysis of crystallization processes, that do not involve any mass change or gasses generated, has been explored. The effects in the sample temperature produced by the exothermicity of the crystallization processes are avoided by using the CRTA methodology, since the control of the rate of the process minimizes the heat transfer phenomena. Moreover, the shape of the α-T plots of the CRTA experiments strongly depends on the reaction mechanism, while sigmoidal shape curves are obtained from conventional heating rate procedure, whatever is the reaction mechanism.

A custom method has been programmed, employing the software of a commercial simultaneous TG/DSC instrument, to perform constant rate thermal analysis using the heat flow as the control signal representative of the rate of the process. The method is easily implemented just by using an especial procedure described here.

The CRTA control system has been successfully tested with the kinetic study of the thermal crystallization of a zirconia gel employing a single CRTA curve. It has been proven that the crystallization obeys an Avrami-Erofeerv kinetic model since the curve presented a minimum in the temperature-time profile. The differential model-fitting method applied to the CRTA curve confirmed the kinetic model, and values of activation energy of 220 kJ mol^{-1} and preexponential factor of 5.90×10^{15} min^{-1} were obtained for the process.

It is consequently demonstrated that a single curve recorded under CRTA conditions is enough to discriminate between the different kinetic models for crystallization processes, which cannot be done in linear heating experiments, and reliable kinetic parameters can be determined.

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Figure captions

Figure 1. Kinetic curves simulated for four kinetic models considering an activation energy of 125 kJ mol^{-1} and pre-exponential factor of 10^{12} min^{-1}. (a) Curves constructed assuming a linear heating rate of 5 K min^{-1} and (b) Curves obtained considering a constant rate of 10^{-3} min^{-1}.

Figure 2. Experimental DSC peak for the thermal crystallization of the dried zirconia gel registered at the conventional heating rate of 1 K min^{-1}.

Figure 3. Experimental α-T kinetic curve registered at 1 K min^{-1} for the thermal crystallization of the zirconia gel fitted employing the differential model-fitting method with four different kinetic models.

Figure 4. Flowchart of the CRTA in the DSC experiment.

Figure 5. Experimental temperature profile and heat flow curve against time obtained for the crystallization of the zirconia gel in CRTA conditions.

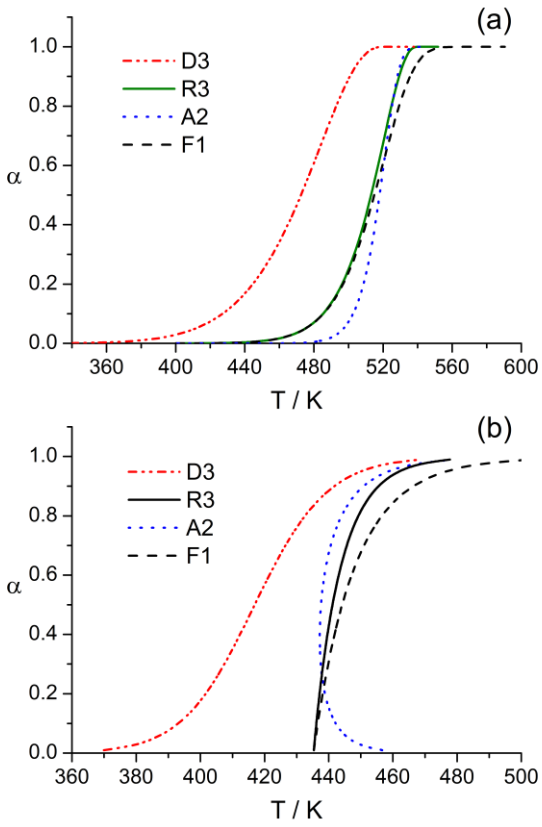
Figure 6. (a) DSC traces for the experiments performed in linear heating and in CRTA conditions. (b) Corresponding derivatives of the heat flow.

Figure 7. Experimental kinetic curves obtained for the thermal crystallization of the zirconia gel in CRTA conditions at a rate of 8×10^{-3} min^{-1}. (a) Conversion, temperature and rate of the process against time. (b) Conversion versus temperature (dots) and simulated curve using the kinetic parameters resulting from the kinetic analysis (solid line).

Figure 8. Plots obtained from fitting the DSC trace for a CRTA experiment to four kinetic models employing the differential model-fitting method (equation 2) described in the theoretical section.

Table 1. Kinetic functions corresponding to the most used kinetic models.

Mechanism	Symbol	f(α)
First order	F1	$(1-\alpha)$
Phase boundary controlled reaction (contracting area)	R2	$(1-\alpha)^{1/2}$
Phase boundary controlled reaction (contracting volume)	R3	$(1-\alpha)^{2/3}$
Random nucleation and growth of nuclei through different nucleation and nucleus growth models (Avrami-Erofeev eq n ≠ 1)	An	$n(1-\alpha)[-\ln(1-\alpha)]^{1-\frac{1}{n}}$
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$
Three-dimensional diffusion (Jander eq)	D3	$3(1-\alpha)^{2/3}/\left[2(1-(1-\alpha)^{\frac{1}{3}})\right]$
Three-dimensional diffusion (Ginstling-Brounshtein eq)	D4	$3/\left[2((1-\alpha)^{-1/3}-1)\right]$



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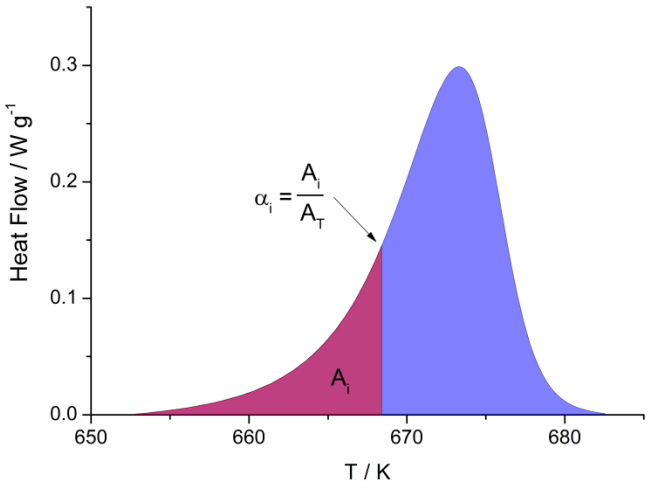

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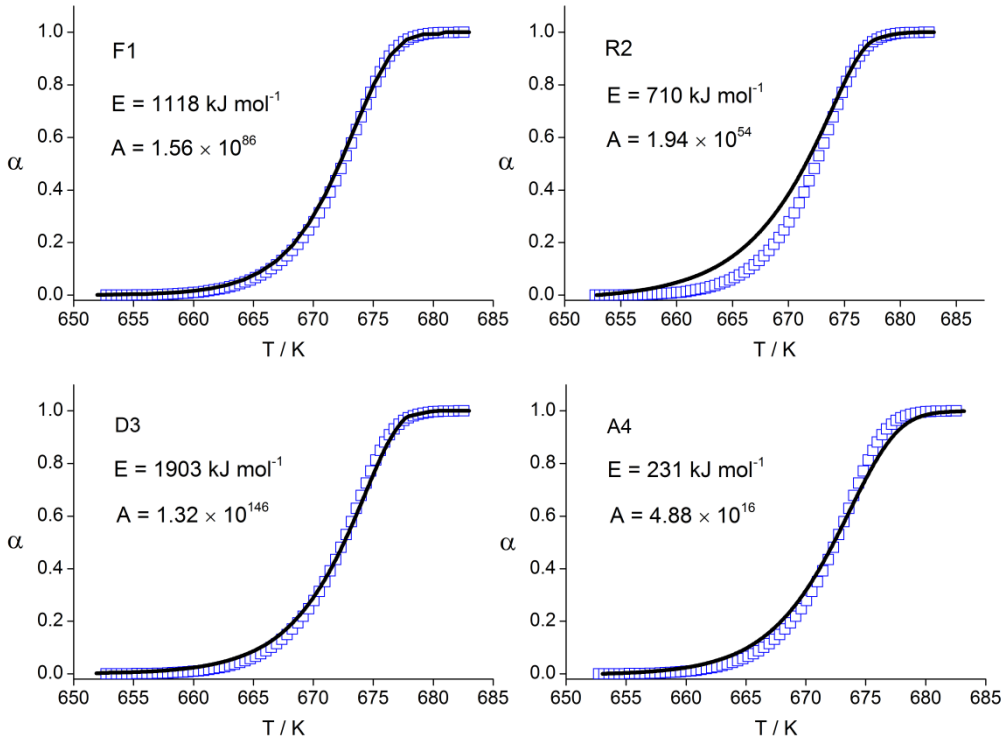

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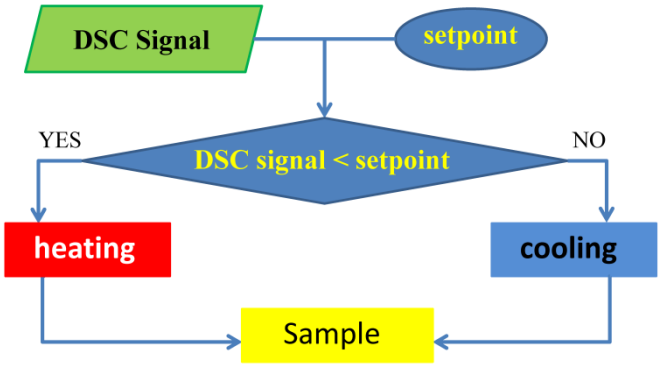

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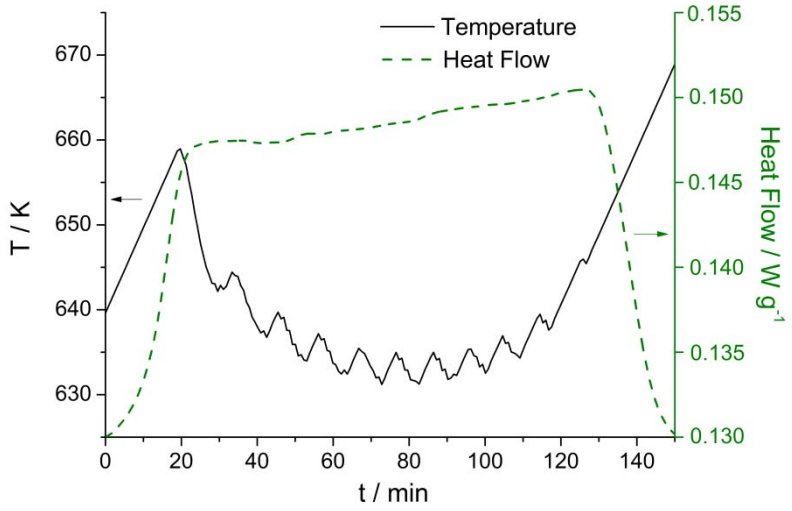

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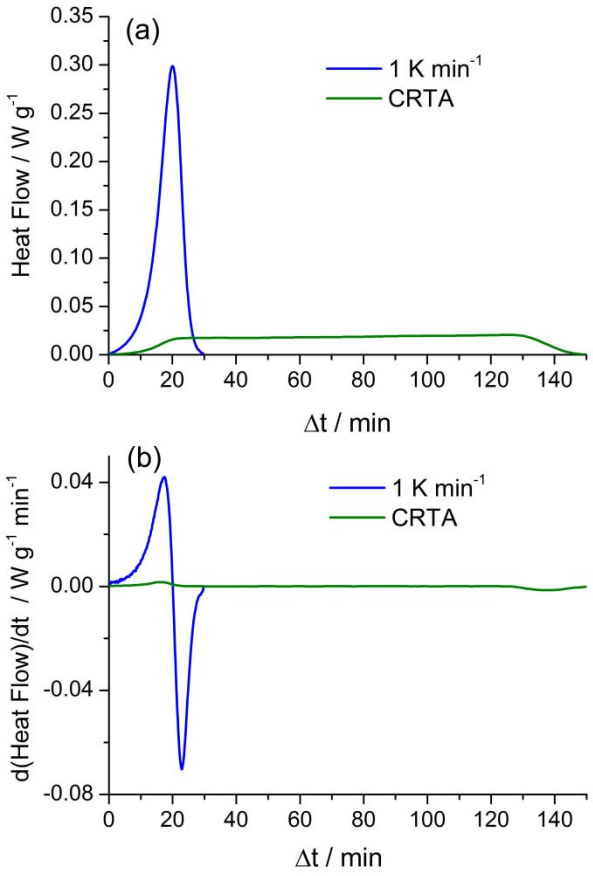

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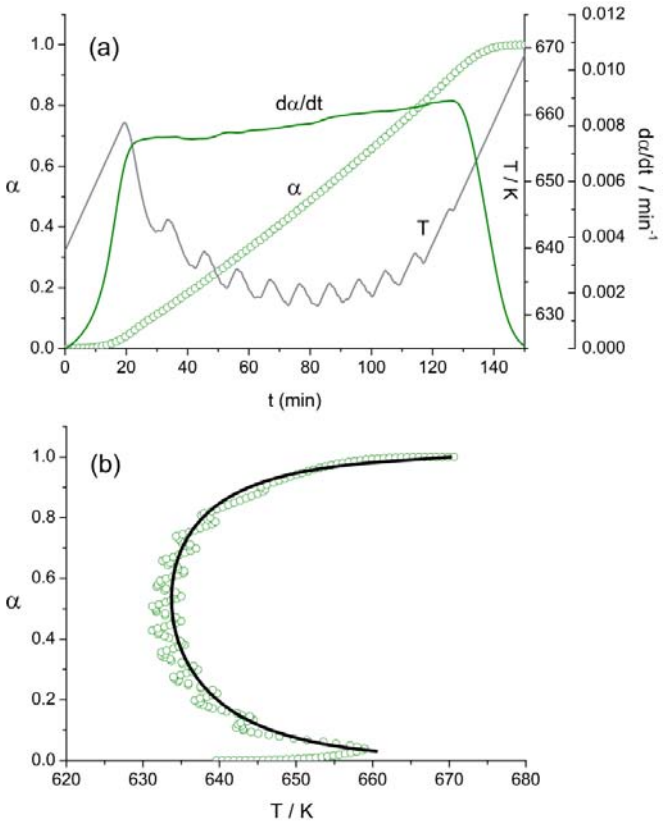

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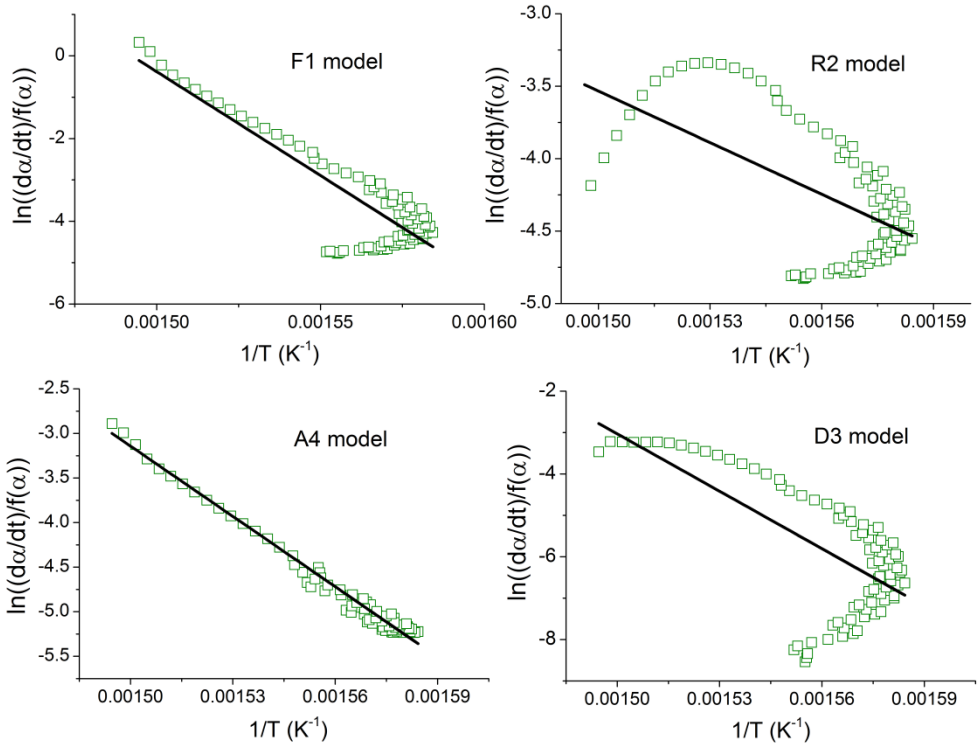

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